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Research on New Solid State Defect Structures Based on WO_3 and on V_2O_5

By

M. J. Sienko

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M. J. Sienko, Principal Investigator

Cornell University, Department of Chemistry

Solid State Sciences Division

Air Force Office of Scientific Research

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Summary:

This project was initiated to follow up the discovery that in the tungsten bronze series (M_xWO_3, $0 < x < 1$, M = univalent metal) the copper tungsten bronzes (M = Cu) behaved as semiconductors whereas the alkali tungsten bronzes were metallic. Since the properties of the alkali tungsten bronzes were consistent with an "electron-gas" model (M atoms in a WO_3 matrix completely ionized to give M^+ and free electrons) the anomaly of the Cu_xWO_3 behavior suggested a finite excitation energy for getting carriers into the conduction band -- an excitation energy which might be a function of the ionization potential of M. Thus, there was the interesting possibility that with appropriate choice of M in WO_3 one might develop an entire series of materials, based on the same host matrix, which would represent a continuous gradation in properties from insulating to metallic. However, there was the immediate contradiction that the observed magnetic susceptibility of Cu_xWO_3 was too low to support the idea of finite concentrations of non-ionized Cu° atoms in WO_3. Therefore, the problem started as a simple attempt to define what were the current carriers in Cu_xWO_3, what was their concentration, and what was their mobility as a function of temperature. As parallel investigations, Ag_xWO_3 and Li_xWO_3 were studied for the same parameters since they too had been reported to be semiconductors.

As the problem unfolded it became obvious that carrier characteristics in M_xWO_3 were almost exclusively determined by the host structure WO_3, so a careful study of single crystals of WO_3 was initiated. The ultimate result was that for M_xWO_3 quantitative justification can now be given to the whole range of solid state properties investigated -- viz., Hall mobility, resistivity, thermoelectric power, magentic susceptibility, magnetic resonance -- both as a function of temperature and as a function

of composition.

In order to account for the relatively high mobility of carriers in M_xWO_3, it was most fruitful to consider that the conduction band in WO_3 arises from overlap of the $5d(t_{2g})$ orbitals of the tungsten atoms. Because the spatial extent of such orbitals decreases as the principal quantum number but increases with decreasing atomic number, it was believed that overlap of the $3d(t_{2g})$ orbitals of vanadium in V_2O_5 might also lead to a conduction band of finite width as in WO_3. To this end we have prepared single crystals of V_2O_5 doped with Na, Li, or Cu and have investigated their electric and magnetic properties. This phase of the work is still in progress but present indications are that the $M_xV_2O_5$ systems are quite different from the M_xWO_3 systems in that electrons are localized in the former but not in the latter.

Personnel:

The people who have been involved in this project include the following:

(a) Research Associates:

B. R. Mazumder	(6-16-58) - (8-31-59)
B. Banerjee	(3-16-59) - (9-30-60)
J. Ragle	(9-1-60) - (8-31-62)

(b) Research Assistants:

Julien Gendell	Harolyn Perkins
Frank Holly	Joan Cloonan
Jerome Sohn	
Paul Weller	
Thu Ba Truong	
Daniel Kudrak	
Sheila Morehouse	

(c) Lab Technicians:

Judith (Grove) Koch
Allen F. Podell
John Raymonda
Sheila Morehouse

Earned Advanced Degrees:

Five of the nine research assistants have earned advanced degrees from Cornell as follows:

(a) Julien Gendell - Ph.D. - Jan. 1962 - "Magnetic Resonance Studies of Some Vanadium Bronzes".

(b) Frank Holly - Ph.D. - June 1962 - "Surface Tension of Solutions of Alkali Metals in Ammonia".

(c) Paul Weller - Ph.D. - Jan. 1962 - "Solid State Studies of Copper Tungsten Bronze".

(d) Thu Ba Truong - M.S. - June 1960 - "The Lithium Tungsten Bronzes: Preparation and Determination of Electrical Conductivities".

(e) Sheila Morehouse - M.S. - June 1962 - "The Potassium and Rubidium Tungsten Bronzes: Determination of Electrical Conductivities and Magnetic Susceptibilities".

Jerome Sohn, Daniel Kudrak, and Harolyn Perkins have completed substantial parts of their work toward Ph.D. degrees, which will probably be awarded in 1963.

Publications:

The record of the project is substantially given by the articles which have appeared in the literature, by those now in press, and those which will appear in the future. These include the following:

(1) "Thallium - Tungsten Bronze: A Solid State Defect Structure" - M. J. Sienko - J. Am. Chem. Soc., 81, 5556 (1959).

Thallium-Tungsten bronzes, Tl_xWO_3 have been prepared ranging in composition from x = 0.19 to x = 0.36. Preparation methods included: (1) heating Tl_2WO_4 and W; (2) vapor phase reaction of Tl and WO_3; (3) electrolysis of Tl_2CO_3 and WO_3 mixtures. Products were crystalline and powder diagrams could be indexed in the tetragonal system with a = 7.31 Å. and c = 12.80 Å. Electrical resistance measurements using a potential probe method on single crystals indicated metallic conduction with specific resistivity varying from 6.0×10^{-3} ohm-cm. at 25° to 9.0×10^{-3} ohm-cm. at 240°. Thermoelectric power at room temperature was -20 microvolts per degree referred to platinum, suggesting one free electron per thallium atom. A general model is proposed for the tungsten bronzes M_xWO_3 where M is viewed as giving rise to local energy levels in the forbidden gap between the conduction and valence bands of WO_3.

(2) "Some Solid State Studies of Silver-doped WO_3" - M. J. Sienko and B. R. Mazumder - J. Am. Chem. Soc., 82, 3508 (1960).

A material corresponding to $Ag_{0.10}WO_3$ has been isolated from the thermal equilibration of WO_3 with various sources of silver. Single crystal studies indicate that it is orthorhombic (a = 7.35, b = 3.73 and c = 3.85 A.) and that it conducts as a metal between 25 and 600° (specific resistivity increases linearly from 0.072 ohm-cm. at 25° to 0.155 ohm-cm. at 600°). The electron mobility at 25° is 0.44 cm.^{2}/volt sec., which is approximately the same as that previously observed in thallium tungsten bronze. It is proposed that $Ag_{0.10}WO_3$ represents a defect structure in which a 5 d conduction band of WO_3 is populated by electrons from the silver atoms and in which a more symmetric structure of WO_3 has been stabilized by configurational entropy.

(3) "Studies in Non-Stoichiometry. Electrical Conductivity and Carrier Mobility in Lithium Tungsten Bronzes" - M. J. Sienko and Thu Ba Nguyen Truong - J. Am. Chem. Soc., 83 3939 (1961).

Single crystal resistivity measurements, X-ray spacings, and densities are reported for three lithium tungsten bronzes: $Li_{.384}WO_3$, $Li_{.377}WO_3$, and $Li_{.365}WO_3$. In the range -150 to 90°, conduction is metallic, in contradiction to previous reports. The electron mobility increases with lithium content and decreases with temperature. Arguments are given for believing there should be a transition from localization of electrons to delocalization at approximately $Li_{.25}WO_3$. Reexamination of previously reported magnetic results suggests a maximum in the effective mass of the carriers at $M_{.30}WO_3$. The change in effective mass and mobility is attributed mainly to the effect of cationic point charge defects on the 5d conduction band.

(4). "Studies in Non-Stoichiometry. Magnetic Susceptibilities in the Tungsten-Oxygen System" - M. J. Sienko and B. Banerjee - J. Am. Chem. Soc., 83, 4149 (1961).

Magnetic susceptibilities have been measured by the Gouy method for several tungsten oxides of the series WO_x. At 297.5°K the susceptibility per unit volume is found to increase monotonically from -0.65×10^{-6} to $+0.46 \times 10^{-6}$ as x in WO_x decreases from 3 to 2. Results are interpretable in terms of a defect structure in which 3 - x oxygen atoms have been removed from a host WO_3 lattice leaving 2(3 - x) electrons in the conduction band of the host. Quantitative agreement with a Pauli-Peierls calculation is surprisingly good. The model may be applicable to other non-stoichiometric oxides for which "mixed-oxidation-state" structures have been postulated.

(5) "Anisotropy of Nuclear Magnetic Resonance in Vanadium Pentoxide" - J. L. Ragle - J. Chem. Phys. 35 753 (1961).

The NMR spectra of V^{51} in V_2O_5 at high fields show a marked symmetry of the central component, originating in an anisotropic magnetic shielding. The observed anisotropy is attributed to excited states.

(6) "Carried Characteristics in Copper-doped WO_3 from Conductivity, Hall voltage, and thermal e.m.f. Studies" - M. J. Sienko and Paul Weller - Inorg. Chem. 1 324 (1962).

Single crystals of $Cu_{0.078}WO_3$, $Cu_{0.094}WO_3$, and $Cu_{0.25}WO_{3+\delta}$ have been prepared by thermal decomposition of $CuWO_4$ and WO_3. Potential-probe resistivity measurements in the range 120 to 770°K. indicate complex semi-conducting behavior. $Cu_{0.094}$, which is orthorhombic, shows three linear segments in the log ρ vs. 1/T dependence, the apparent activation energies being 0.05 e.v. below 170°K., 0.4 e.v. between 170 and 220°K., and 0.45 e.v. above 500°K. Between 220 and 500°K., behavior is "metallic". $Cu_{0.25}WO_{3+\delta}$ which is triclinic, shows no metallic region but has two linear segments with activation energy 0.10 e.v. below 700°K. and 0.15 e.v. above. Measurements of the Hall voltage and of the thermoelectric power indicate that carries are electrons. At 300°K., representative carrier densities are 5×10^{18}, and 1×10^{18} electrons/cc. with mobilities 6, 10, and 0.4 $cm.^2/v.sec.$ for $Cu_{0.078}WO_3$, and $Cu_{0.094}WO_3$, and $Cu_{0.25}WO_{3+\delta}$, respectively. Thermal e.m.f. values fall in the range -220 to -300 $\mu v./deg.$ Results are interpreted in terms of a conduction band model with destruction of the band below room temperature due to a probable ferroelectric transition in the host lattice. Excess oxygen acceptor centers of appreciable ionization energy apparently are present in small concentration in the low-copper materials and in large concentration in the high-copper material.

(7) "Magnetic Resonance Studies of Lithium Vanadium Bronze" - Julien Gendell, R. M. Cotts, and M. J. Sienko, J. Chem. Phys. 37, 220 (1962).

The nuclear magnetic resonance of Li^7 in $Li_xV_2O_5$ shows no Knight shift, but there is a small diamagnetic shift relative to LiCl solution, amounting to 0.0023 and 0.0058% at 296° K and 77° K, resp. The spin-lattice relaxation time, T_1, as measured by pulse experiments, decreases from 0.16 sec. at 296°K to a minimum of 0.060 sec. at 163 °K and then rises to 0.13 sec. at 77° K. The free induction decay half-width decreases from 850 μsec. at 296° K to 100 μsec. at 77° K. The minimum in T_1 is attributed to back-and forth motion of the lithium ions within but normal to the axis of channels in the oxygen framework; the line narrowing, to diffusion along the channel from one unit cell to an adjacent one. EPR studies give Lorentzian-shaped lines, centered at g = 1.96, of intensity proportional to 1/T. Results are consistent with a model in which lithium atoms in a host V_2O_5 structure are completely ionized to give Li^+ ions and electrons which are almost but not completely localized as V^{+4} centers.

(8) "The Electrical and Magnetic Properties of the Tungsten and Vanadium Bronzes" - M. J. Sienko - in press for November 1962 publication in Advances in Chemistry.

The metallic properties of the tungsten bronzes, M_xWO_3, are discussed in terms of a band model in which a conduction band resulting from overlap of the 5d(t_{2g}) orbitals of the tungsten is populated by donor atoms M. Optical properties and magnetic susceptibilities are consistent with the model. The apparent semiconductivity in Cu_xWO_3 and Ag_xWO_3 is attributed to second order transitions in the host WO_3 structure. The non-stoichiometric oxides WO_3-δ can also be interpreted in terms of the same band model with each oxygen defect δ contributing two electrons

to the conduction band. The vanadium bronzes, $M_xV_2O_5$, are more complicated in that the carriers are more localized, giving rise to higher magnetic moments and a lower conductivity which is anisotropic and not metallic. NMR experiments on $Li_xV_2O_5$ give no Knight shift but a line-narrowing which indicates diffusional motion of Li. Pulse decay experiments suggest an oscillating motion of Li in the tunnels of the oxyvanadium network at lower temperatures than those at which diffusion along the tunnels is initiated.

(9) "Electron Spin Resonance Study of Partially Reduced Vanadium Pentoxide" - J. L. Ragle - submitted to J. Chem. Phys.

Single crystals of partially reduced vanadium pentoxide have been prepared in the form $Cu_xV_2O_5$ with $0 \leq x \leq 0.040$, and two distinct types of paramagnetic species have been observed by ESR techniques at X- and K-band frequencies. Neither of these species is associated with copper (II). For $0 \leq x \leq 0.0058$, the dominant species is one in which the electron is localized, hyperfine structure indicating interaction with two equivalent vanadium nuclei. For this species, at $x = 0.0042$ and 77°K, $A = 83.6 \pm 2.0$ gauss, $g_{\parallel} = 1.90$, 1.92 (apparently two similar species), $g_{\perp} = 1.98$. Hyperfine structure is not resolved for static fields not parallel to the crystallographic b-axis, the axis of symmetry of the g-tensor. For $0.0078 \leq x$, the spectra show a superimposed narrow unstructured line of total width 10-20 gauss, with $g_{\parallel} = 1.93$, $g_{\perp} = 1.98$. The large g-shift of this latter species shows that it is still primarily associated with the vanadium sites, but the lack of hyperfine structure indicates a considerable mobility. The g-tensor is again axial about the b-axis of the V_2O_5 lattice.

X-ray powder spectra taken on samples of $Cu_xV_2O_5$ for x = 0, 0.0058, and 0.0114 show no observable differences in lattice parameters.

(10) "Electrical and Magnetic Properties of Potassium Tungsten Bronze and Rubidium Tungsten Bronze" - M. J. Sienko and Sheila Morehouse - submitted to Inorganic Chemistry.

Single crystal conductivities have been measured for $K_{0.40}WO_3$ and $Rb_{0.32}WO_3$ in the range 150 to 370°K. Carrier mobilities, which are somewhat higher than in the Li and Na tungsten bronzes, closely follow a T $\sinh^2$ (θ/2T) dependence. Calculations on the basis of the theory of Howarth and Sondheimer strongly support the assumption that the thermal part of the carrier mobility in the tungsten bronzes is primarily determined by polar scattering from optical mode lattice vibrations. Magnetic susceptibilities have also been measured at room temperature for $Rb_{0.26}WO_3$ and $K_{0.23-0.45}WO_3$. Results are as predicted by the Pauli-Peierls theory for quasi-free electrons.

(11) "Some Solid State Studies of Tungsten Trioxide and the Significance to Tungsten Bronze Theory" - Billy L. Crowder and M. J. Sienko - submitted to J. Chem. Phys.

The Hall voltage, resistivity, and thermoelectric power have been measured on single crystals of tungstic oxide (γ-phase: 10°C to 330°C.). The electrical transport properties can be explained quantitatively on the basis of a shallow donor model (E_D = 0.04 eV) in which carrier mobility is limited primarily by polar scattering from optical mode lattice vibrations. The interaction between electron and phonon is describable by the perturbation theory of Howarth and Sondheimer (replacing the effective mass by the polaron mass) or by the intermediate coupling theory of Lee,

Low, and Pines. The model has been extended successfully to calculate the thermal and composition dependences of resistivity and Seebeck coefficient for the cubic sodium tungsten bronzes. A density-of-states function, based on the change of the effective mass of the conduction electrons with energy as required by the analysis above, gives agreement (for moderate values of x) with existing electronic specific heat data and magnetic susceptibility measurements.

(12) "Surface Energy as a function of composition in the Li-, Na-, and K-NH_3 Systems" - F. Holly and M. J. Sienko - Work completed, manuscript in process, probably for J. Chem. Phys.

The surface energy of lithium, sodium, and potassium in ammonia was measured as a function of concentration. Results show there to be a continuous gradation in $\Delta\gamma$ from electrolytic to metallic behavior. From the first virial coefficient of the $\Delta\gamma$ vs. c expansion, the polarizability of the electron in the dielectric has been calculated.

(13) "Low Temperature Studies of Tungsten Trioxide" - B. L. Crowder and M. J. Sienko, in manuscript, probably for J. Chem. Phys.

Discontinuities in the electrical resistivity, Hall voltage, and thermoelectric power are observed at phase transition temperatures, but with considerable hysteresis depending on the domain characteristics. Low level oxygen removal destroys the β-to-α transition at -40°C.

Unfinished work:

Problems which are not quite complete, on which work will continue under Air Force grant AF-AFOSR-62-218, include the following:

(a) "Low temperature magnetic studies of sodium vanadium bronze" - J. Sohn.

(b) "ESR study of Mn site location in doped zinc orthosilicate" - H. Perkins.

(c) "Magnetic and Electric Properties of Ta_2O_{5-x} and $M_xTa_2O_5$" - D. Kudrak.

Publications on these three problems are expected during the academic year 1962-63.

Equipment:

The items purchased under this contract, most of which are in quite useable condition, have given us a solid state chemistry group as strong as might be found in any chemistry department in the U.S. Because we are continuing to make full use of these instruments and because we intend to pursue even more intensively solid state investigations, we are requesting that the items purchased under contract AF 49(638)-191 be transferred to grant AFOSR-62-218 so as to remain available to our group.

Acknowledgment:

It is a pleasure to express here our appreciation to the Air Force Office of Scientific Research for its broad support of our research efforts. Not only has this support resulted in significant discoveries that improve our fundamental knowledge of solid state materials, but also it has led to the training of several advanced students who are likely to make major scientific advances in the future. Further, it has given our research program a momentum which augurs well for the future.

M. J. Sienko